Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 751

Chemical Modification of Lignin-Rich Paper
Light-Induced Changes of Softwood and Hardwood Chemithermomechanical Pulps: The Effect of Irradiation Sources

M. Paulsson and A.J. Ragauskas

September 1998

Submitted to
Lignin Book
ACS Sympoisum Series
1998

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is an independent graduate school, research organization, and information center for science and technology mainly concerned with manufacture and uses of pulp, paper, paperboard, and other forest products and byproducts. Established in 1929, the Institute provides research and information services to the wood, fiber, and allied industries in a unique partnership between education and business. The Institute is supported by 52 North American companies. The purpose of the Institute is fulfilled through four missions, which are:

- to provide a multidisciplinary education to students who advance the science and technology of the industry and who rise into leadership positions within the industry;
- to conduct and foster research that creates knowledge to satisfy the technological needs of the industry;
- to serve as a key global resource for the acquisition, assessment, and dissemination of industry information, providing critically important information to decision-makers at all levels of the industry; and
- to aggressively seek out technological opportunities and facilitate the transfer and implementation of those technologies in collaboration with industry partners.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

Chemical Modification of Lignin-Rich Paper

Light-Induced Changes of Softwood and Hardwood Chemithermomechanical Pulps: The Effect of Irradiation Source

Magnus Paulsson[1] and Arthur J. Ragauskas[2]

[1]Chalmers University of Technology, Department of Forest Products and Chemical Engineering, S-412 96 Göteborg, Sweden
[2]Institute of Paper Science and Technology, Chemical and Biological Sciences Division, 500 10th Street, N.W., Atlanta, GA 30318, USA

Light-induced brightness reversion is currently a topic of considerable interest for the pulp and paper industry. The objective of this study was to describe the effect of using different irradiation sources on the accelerated photoyellowing properties of untreated and chemically modified bleached high-yield pulps. The wavelength distribution of the irradiation source strongly influenced the photochemistry of both untreated and acetylated pulps. UV/VIS absorption difference spectra of aspen chemithermomechanical pulp (CTMP), irradiated with broad-band UV-radiation, exhibited an apparent absorption maximum at 370 nm with a shoulder at 415 nm, whereas the aspen CTMP aged with the UV/VIS-fluorescent lamps exhibited an absorption peak at 360 nm and substantially less absorption in the entire visible region (λ>400 nm). Two major absorption peaks, at 330-345 nm and at 425 nm, were observed in the absorption difference spectra of irradiated spruce CTMP regardless of the irradiation source used. However, in addition to the photodiscoloration, photobleaching with λ_{max}~390 nm was observed when the spruce CTMP was irradiated with the UV/VIS-fluorescent lamps. Acetylation was found to slow down the UV-light induced reactions, but could also promote photobleaching reactions when the pulps were subjected to an irradiation source emitting light in the visible range. Generally, no further discoloration was observed when the acetylated CTMPs (acetyl content, 8-10%) were irradiated with the UV/VIS-fluorescent lamps under the aging conditions used in this work. This investigation has shown the importance of choosing a light source that resembles the actual reversion situation as closely as possible (e.g., contains both an ultraviolet and a visible component) if realistic accelerated light-induced reversion conditions are to be obtained.

The use of mechanical and chemimechanical pulps as constituents in higher grades of printing paper is severely restricted by the rapid color reversion (yellowing) that occurs upon exposure to daylight or indoor illumination. This phenomenon has been attributed to a light-induced oxidation of the lignin present in the pulp. Extensive and comprehensive research, performed during the last decade, has given not only new

information about the photochemical reactions causing yellowing, but also information on the potential photostabilizing methods, although no single approach so far has become technically or economically feasible to meet all the needs of the paper industry. Heitner and Schmidt (*1,2*) and Leary (*3*) have summarized current knowledge in this field in comprehensive literature reviews.

The photochemical changes that occur during irradiation of lignin-rich pulps do not involve only discoloration reactions. Several researchers have reported a photobleaching effect when pulps were irradiated at longer wavelengths, i.e., visible light (*4-9*). If the color-forming reactions could be eliminated or slowed down, the bleaching reactions would predominate and result in a brightness increase for high-yield pulps when irradiated in daylight. However, the darkening reactions normally dominate over the brightening reactions, and the net result is a discoloration of the lignin-rich material.

Exposure of CTMP (chemithermomechanical pulp) and TMP (thermomechanical pulp) to ultraviolet radiation with a wavelength of 300-400 nm produced chromophores with absorption maxima at 350 and 420 nm (*10*). These chromophores were considered to be a methoxy-*p*-benzoquinone and an *ortho*-quinone with an aliphatic substituent in the 2-position. Structures of the *ortho*-quinonoid type have been detected in different types of high-yield pulps, both before and after irradiation. Lebo et al. (*11*) found that about 75% of the increase in color during irradiation of white spruce refiner mechanical pulp was caused by the formation of *ortho*-quinones. Zhu et al. (*12*) used fluorescence spectroscopy to confirm the presence of photochemically generated *ortho*-quinones in several hydrogen-peroxide-bleached high-yield pulps. Schmidt et al. (*13*) reported that both methoxylated and unmethoxylated *ortho*-quinones were likely to be introduced in peroxide-bleached mechanical pulps during irradiation. Monomeric *ortho*-quinones were suggested to be the major chromophores formed during light-induced yellowing of lignin-rich pulps based on UV/VIS reflectance spectroscopy of peroxide-bleached GWP (groundwood pulp), CTMP, and quinonoid lignin model compounds (*14*). Stilbene *ortho*-quinones were reported to be the only colored products formed when monohydroxystilbenes (deposited on the surface of a filter paper) were exposed to UV-radiation (*15*). Furthermore, the chromophores produced by UV-radiation were found to be almost completely removed by sodium borohydride reduction (*16-19*). This suggests that most of the colored substances formed contain carbonyl structures (quinones, conjugated ketones, aldehydes) that can be reduced by $NaBH_4$.

Argyropoulos et al. (*20*) used solid-state ^{31}P NMR spectroscopy on samples of irradiated unbleached and hydrogen-peroxide-bleached GWP (oxyphosphorylated) in order to determine the early photochemical changes that occur during light-induced yellowing. The data suggested that *ortho*-quinones initially produced during irradiation subsequently reacted to form more complex carbonyl chromophoric structures which do not have a quinonoid character. It was also found that *ortho*-quinones were converted faster in the unbleached pulp than in the peroxide-bleached pulp. The bleached pulp contains more stilbenes that could be converted to stilbene *ortho*-quinones during irradiation (*15*), and it is possible that these structures require longer irradiation times to be eliminated. The conversion of quinones to more complex chromophores could explain why no quinones or quinonoid structures were detected in irradiated milled wood lignin (MWL) (*21*).

Forsskåhl and Janson (*6*) reported that the two main chromophores (displaying bands at 370 and 430 nm), generated by irradiation of chemimechanical pulps, were interrelated. Irradiation at a short wavelength (373 nm) creates a colored chromophore, while irradiation at the longer wavelength (435 nm) leads to the formation of a colorless product. These authors suggest that there are several possible candidates for such a system; a hydroquinone-quinone system, charge transfer complexes, possibly quinone methides and also cis-trans isomerism of aromatic conjugated double bonds. The same effect was later found for irradiated unbleached and peroxide-bleached

thermomechanical pulps (*22*). Schmidt et al. (*13*) reported that methoxylated *ortho*-quinones could be bleached by 420 nm irradiation, whereas unmethoxylated *ortho*-quinones sensitized destruction of aromatic groups. Robert and Daneault (*23*) observed two major absorption peaks at 360 and 425 nm when TMP paper (black spruce/balsam fir mixture) was exposed to UV light (λ, 300-400 nm). The peak at 360 nm was the result of the disappearance of one chromophore and the appearance of a different chromophore. The other peak (at 425 nm) was the result of the formation of three chromophores. It is important to bear in mind that structures of the quinonoid type are themselves photosensitizers and they can thus contribute to further chromophore formation (*24-28*).

The present communication describes the effect of irradiation sources with different wavelength distributions on the light-induced yellowing of untreated and acetylated hydrogen-peroxide-bleached aspen CTMP and spruce CTMP, the pulps most often suggested as replacement for chemical pulps in high-quality paper grades. The mechanism of stabilization (and yellowing) has been studied using solid-state UV/VIS diffuse reflectance spectroscopy performed on high basis weight (200 g/m^2) handsheets.

Experimental

Pulps and Paper Samples. Commercially produced hydrogen-peroxide-bleached spruce (*Picea abies*) CTMP and hydrogen-peroxide-bleached aspen (*Populus tremuloides*) CTMP were used as received for the studies described in this paper. The pulps were obtained as dried samples. The high-brightness hardwood CTMP was manufactured employing hydrogen peroxide both as a chemical pretreatment and as a bleaching stage. Handsheets [60 or 200 g/m^2 (for UV/VIS spectroscopy)] were prepared according to TAPPI Test Method T 205 om-88. The paper sheets were then conditioned at 23°C and 50% R.H. according to TAPPI Test Method T 402 om-88 before further treatment.

Acetylation Procedure. The handsheets [cut into strips (30 x 75 mm)] were acetylated (at 100 or 110°C) according to the procedure previously described (*29*). The acetyl content was calculated from the amount of acetate liberated after saponification with sodium hydroxide (*30*). The acetyl content is given as a percentage of the dry weight of the paper.

UV/VIS Diffuse Reflectance Spectroscopy. UV/VIS spectra were recorded on a Perkin Elmer Lambda 19 DM spectrophotometer equipped with a diffuse reflectance and transmittance accessory (Labsphere RSA-PE-90). The accessory is essentially an optical bench which includes double beam transfer optics and a six-inch diameter (154 mm) integrating sphere. Background correction was made with a SRS-99-010-7890 standard. The absorbance (*ABS*) was calculated from the diffuse reflectance (R_∞) using the following expression derived from the Beer-Lambert law (cf. *23*): $ABS = -\log R_\infty$. The resulting spectra were averaged from four to six measurements.

Accelerated Light-Induced Yellowing. The paper samples were subjected to accelerated photoyellowing in a Rayonet photochemical reactor (Model RPR 100, The Southern New England Ultraviolet Company, Branford, CT, USA) equipped with eight RPR 3500Å UV-fluorescent lamps ("blacklight," The Southern New England Ultraviolet Company) or eight RPR 5750Å UV/VIS-fluorescent lamps (The Southern New England Ultraviolet Company) and a merry-go-round apparatus for uniform irradiation. Accelerated reversion studies were also conducted with a SUNTEST CPS (Heraeus HANAU, Hanau, Ger.) light-aging tester equipped with a xenon lamp (nominal rating of xenon burner, 1.1 kW) and filters (ultraviolet and window-glass),

which eliminate radiation of wavelengths below 310 nm. The irradiance was controlled by an optical sensor that compensates for possible main voltage fluctuations and burner aging. The temperatures during irradiation were 29, 27, and 30°C for the UV-fluorescent lamps, UV/VIS-fluorescent lamps, and xenon lamp, respectively. The use of controls in each irradiation experiment and the exchange of UV/VIS-fluorescent lamps between aging series were done to monitor and minimize the effects of aging of the light sources studied.

Optical Measurements. TAPPI brightness was measured using a Technidyne Brightimeter (Model S-5) according to TAPPI Test Method T 452 om-92. The reflectance of a single sheet of paper (60 g/m^2) over a completely black, nonreflecting surface (over a hollow black body, reflectance <0.5%) and the reflectance over a stack of paper (high enough to inhibit any transparence of light) were recorded. The specific light scattering coefficient (s, at 457 nm) was then calculated using the Kubelka-Munk theory. Optical properties of the SUNTEST CPS irradiated handsheets were measured using an Elrepho 2000 spectrophotometer. The post color (PC) number at 457 nm (*31*) was calculated for the acetylation treatment (PC_1) and for the light-induced reversion (PC_2) (cf. *32*). The sum of PC_1 and PC_2 represents the total effect of the treatment: $PC = PC_1 + PC_2$. The change in specific light-absorption coefficient (Δk, at 457 nm) during irradiation was calculated from the PC_2-value with the assumption of constant light scattering (*33*).

Results and Discussion

Light Sources. To assess the importance of the wavelength distribution of irradiation sources used for accelerated reversion tests, a series of handsheets made from untreated and acetylated high-yield pulps were irradiated with three different light sources and the optical properties monitored. The light sources chosen were UV-fluorescent lamps, UV/VIS-fluorescent lamps, and a xenon lamp, i.e., commonly used irradiation sources in many light-induced aging equipments. The UV-fluorescent lamps emit light in a band between 300 and 420 nm (approximate Gaussian spectral distribution, λ_{max}=350 nm), i.e., the visible component of diffuse sunlight or office light is practically missing (Figure 1a). The UV-fluorescent lamps give an assessment of the UV light-aging properties and could be useful when complications from other wavelengths are not desirable. The UV/VIS-fluorescent lamps emit light in the ultraviolet and visible range (from about 350 to 700 nm, λ_{max}=575 nm) and have a comparatively close match to the conventional standard "cool white" fluorescent color used in many commercial lighting installations (Figure 2a). The energy distribution is enriched at 575 nm, i.e., most of the light is emitted in the visible part of the spectrum. The spectral distribution of the transmitted light from the xenon lamp and filter combinations used was similar to that of average indoor daylight (Figure 3a). The spectral distribution of standard "cool white" fluorescent color (*34*) and natural daylight (*35*) is given, as a comparison, in Figures 2a (broken line) and 3a (dotted line), respectively.

Change in Optical Properties During Accelerated Photoyellowing. The pulps chosen for this study were a hydrogen-peroxide-bleached spruce CTMP and a hydrogen-peroxide-bleached aspen CTMP. The optical properties, before and after the acetylation treatment and after the accelerated aging procedure, are shown in Table I.

Unacetylated Pulps. Figures 1b, 2b, and 3b show the effects of different light sources on the photoyellowing properties of untreated pulps. The H_2O_2-bleached spruce CTMP was used as a control to determine the different periods of irradiation that were needed to obtain an approximately equivalent degree of light-induced

reversion under the test conditions used (cf. Table I). The comparison was made at 4, 40, and 216 hours (9 days) for the UV-fluorescent lamps, xenon lamp, and UV/VIS-fluorescent lamps aged sheets, respectively. As can be seen in Figures 1b and 3b, the yellowing of the UV-fluorescent lamps and xenon lamp irradiated sheets is characterized by a rapid initial phase followed by a slower phase. This is the general behavior of the discoloration process that has been reported by several researchers (*26,30,36,37*). When the UV/VIS-fluorescent lamps were used as an irradiation source the initial rapid phase was less pronounced, resulting in flatter brightness curves, especially for the high-brightness aspen CTMP (Figure 2b). The rate of light-induced chromophore formation was significantly lower for the aspen CTMP than for the spruce, and the variation obtained in aging results between the different exposure techniques used was larger. The change in light absorption coefficient (Δk) was between 2.7 and 6.2, i.e., ca. 40 to 75% lower than that for the spruce CTMP (cf. Table I). Hardwood pulps have previously been reported to be more resistant toward light-induced aging than softwood pulps (*32,33,38*). The lower rate of yellowing of hardwoods may be associated, in part, with their lower lignin contents compared to that of softwoods.

Acetylated Pulps. To establish if chemical modification (e.g., acetylation) of the pulps altered the aging response toward the tested irradiation sources, a series of test sheets were acetylated to various degrees. As can be seen in Table I, the acetylation treatment resulted in a small brightness loss for the hydrogen-peroxide-bleached spruce CTMP (about 2.5 brightness units). The brightness loss for the hydrogen-peroxide-pretreated high-brightness aspen CTMP was more severe; an acetylation time of 10 minutes (110°C) resulted in a brightness loss of about 10 brightness units. These findings agree well with results from earlier investigations (*29,* Paulsson, M.; Ragauskas, A.J. *Nord. Pulp Pap. Res. J.*, in press).

As can be seen in Figures 1 to 3 (and Table I), acetylation strongly inhibited the photoyellowing as previously reported (*30,39*). In Figures 1-3, **c** illustrates the effect of light source on the yellowing properties of acetylated, H_2O_2-bleached spruce CTMP sheets. When irradiated with the UV/VIS-fluorescent lamps, photobleaching of the acetylated sheets took place. As expected, the most severe yellowing (no photobleaching) was observed when the CTMP sheets were irradiated with the UV-lamps (emitted almost no light in the visible range). The difference in reverted brightness between the different light sources was about 11 brightness units for the low acetylated pulps (acetyl content of 4.6%) and more than 14 units for the high acetylated pulps (acetyl content, 9.4%, see Table I).

The degree of reversion was in the order UV>xenon>>UV/VIS lamps for the acetylated aspen CTMP (**d** in Figures 1-3), i.e., the same order as for the bleached spruce CTMP. The UV/VIS-fluorescent lamps induced rapid and strong photobleaching of the acetylated samples. The TAPPI brightness was ca. 82% after 24 hours of irradiation for both acetylation levels, which corresponds to a brightness gain of 1 to 7 brightness units, depending on the derivatization degree studied. Thus, most of the colored substances formed on acetylation of hydrogen-peroxide-pretreated aspen CTMP can easily be converted to colorless structures during irradiation with visible light.

The photobleaching (decrease in light absorption at λ_{max}~360 nm) observed on irradiation of MWL and high-yield pulps has been attributed to the photooxidation of coniferaldehyde end groups in lignin to produce vanillin-type end groups (*40,41*). Furthermore, the dissimilarities in the absorption difference spectra of peroxide-bleached softwood TMP and peroxide-bleached softwood CTMP have been explained in terms of coniferaldehyde photobleaching (*18*). It is also possible that quinonoid structures, absorbing in the blue-green region of the spectrum, photochemically convert to colorless structures (for general comments on light-induced reactions of quinones, cf. *42,43*). This has been demonstrated in the case of methoxy-*p*-benzoquinone incorporated in a solid carbohydrate matrix (i.e., 2-

hydroxypropylcellulose); the photoreduction to methoxy-hydroquinone was a rapid process, whereas the photooxidation of the hydroquinone was comparatively slow (*27*). Ragauskas (*44*) reported that simple *para*- and *ortho*-quinones, impregnated onto cellulose sheets, did not generally cause any further darkening during irradiation (photolyzed with a xenon lamp). Several of the examined quinones instead exhibited a small brightness increase in the irradiated sheets, which could possibly be attributed to a photobleaching effect. Furthermore, Schmidt et al. (*45*) found that methoxylated *ortho*-quinones, introduced into thermomechanical pulp by treatment with Fremy's salt, were bleached by 420 nm irradiation, whereas unmethoxylated *ortho*-quinones, generated by treatment with sodium periodate, were not.

Several researchers have reported that methylated and, particularly, acetylated lignocellulosic materials, can be photobleached during irradiation (*39,46-51*). The photobleaching of acetylated materials has been ascribed to the formation of acetyl peroxide or peroxides formed from the carbohydrate acetates during irradiation (*47,50*). When comparing the degree of yellowing of acetylated high-yield pulps aged under different light sources, with the degree of yellowing for untreated high-yield pulps, it is evident that the photostabilization obtained by the acetylation treatment is not only an effect of retarding the color-forming reactions, but is also a result of promoting photobleaching reactions. The results from aging experiments with the UV-fluorescent lamps give an assessment of the UV-light aging properties, i.e., a measurement of the chromophore-retarding effect of acetylation. The photobleaching response of acetylated pulps is illustrated for the sheets aged with the UV/VIS-fluorescent lamps.

It is difficult to explain the photobleaching effect obtained for acetylated mechanical pulps in terms of coniferaldehyde or *ortho*-quinone photobleaching since the amount of these structural units in peroxide bleached lignin is very small. Several investigations have shown that hydrogen peroxide bleaching removes most (but not all) of the coniferaldehyde units in the lignin (*18,52-56*). Furthermore, model compound studies have shown that acetylation rapidly decomposes most of the *ortho*-quinone units, whereas the *para*-quinones were essentially unaffected (*57*). The significance of the remaining coniferaldehyde structures, *ortho*- and *para*-quinones, diguaiacylstilbenes (cf. *58-60*; the term guaiacyl refers to a 4-hydroxy-3-methoxyphenyl residue), or some other still unknown structure for the photobleaching (and brightness stability) needs to be investigated further.

Although the different light sources tested in this investigation gave a comparable degree of reversion for most of the untreated pulps, the effects of different irradiation techniques, i.e., spectral distribution of the light source used, considerably altered the photostabilizing effect obtained by acetylation. The same effect has also been shown for UV-screen treated pulps (Paulsson, M.; Ragauskas, A.J. *Nord. Pulp Pap. Res. J.*, in press). The discrepancy in effectiveness of an inhibiting treatment reported in the literature can, in many cases, be explained in terms of the different exposure techniques used by the researcher/laboratory.

Solid-State UV/VIS Diffuse Absorption Difference Spectroscopy. The interpretation of a UV/VIS absorption spectra at short wavelengths (e.g., below 340 nm) is difficult since the signal-to-noise ratio is low in this region. This is because the paper sample absorbs most of the light due to its thickness and high lignin concentration (*23*). A complement to this study, in the low wavelength range, could be performed using low basis weight sheets, i.e., 10 g/m^2 (cf. *61*). Care should also be taken when evaluating the results after high UV exposures since the assumption of exponential distribution of chromophores in the thickness of the sheet may no longer be valid (*23*). Nevertheless, solid-state UV/VIS diffuse reflectance spectroscopy, performed on thick handsheets and with the consideration of the above limitations, is a powerful technique for the study of light-induced yellowing of lignin-containing

materials. The result that is obtained with this method is what the eye will perceive as "yellowing of a thick paper."

Irradiated Unacetylated Pulps. Figure 4 shows the UV/VIS absorption difference spectra (ΔABS vs. wavelength) of hydrogen-peroxide-bleached aspen CTMP recorded after aging with various light sources. It is evident that the choice of irradiation source strongly influenced the photochemistry. Although both light sources generated a discoloration in the entire visible region (λ>400 nm), the shape of the absorption curves was different. Irradiation with the UV-fluorescent lamps generated an apparent absorption maximum at 370 nm with a shoulder at approximately 415 nm (Figure 4a), whereas the UV/VIS-fluorescent lamps generated an absorption maximum at 360 nm and showed substantially less absorption in the λ>400 nm range (Figure 4b). The spruce CTMP behaved somewhat differently as can be seen in Figure 5. Irradiation with UV-fluorescent lamps generated an apparent maximum at 330 nm and a distinct maximum at 425 nm. The UV/VIS-fluorescent lamps introduced two maxima; one at 330 nm that was shifted toward longer wavelengths (345 nm) after extensive reversion, and one at 425 nm. In addition to the photodiscoloration, photobleaching with λ_{max}~390 nm was observed for the last light source.

Several research groups have used UV/VIS diffuse reflectance spectroscopy to study the yellowing phenomena. Schmidt and Heitner (*18*) reported that hydrogen-peroxide-bleached aspen CTMP showed a single maximum at about 360 nm when exposed to broad-band UV-radiation, but no shoulder at ~415 nm was detected. The high-brightness aspen CTMP used in the present investigation was pretreated with hydrogen peroxide, and it is possible that this treatment changes the chromophoric precursors in such a way that new colored substances, absorbing in the 415 nm region, were formed when subjected to UV-exposure. Generally, UV/VIS diffuse reflectance spectroscopy of hydrogen-peroxide-bleached softwood pulps (GWP, TMP, and CTMP), performed on both thin and thick sheets, shows an increased absorption in the UV region at 320-360 mm and in the visible region at 410-435 nm when exposed to UV-radiation (*10,14,18,23,36,61-67*). The increase in absorption in the UV region has been attributed to the formation of aromatic carbonyl groups (λ_{max}~330 nm) and to the formation of quinones [possibly methoxylated *para*- or *ortho*-quinones (monohydrate adduct see *18*, cf. *68*), λ_{max}~350-370 nm]. It is also possible that coniferaldehyde with an absorption maximum at ~350 nm, generated through photooxidation of coniferyl alcohol, contributes to the UV-absorption peak. The increase in absorption in the visible region is attributed to the formation of chromophores of the *ortho*-quinonoid type, at least in an initial phase.

The present investigation showed that regardless of the wavelength distribution of the irradiation source, absorption peaks appeared in the above-mentioned UV and visible regions during aging of hydrogen-peroxide-bleached spruce CTMP. The relationship between the peak areas and the position of the maxima was, however, dependent on the light source used. The decrease in absorption at 360 nm observed during irradiation of unbleached lignin-containing materials has been attributed to the destruction of coniferaldehyde end groups or to the conversion of quinones to colorless structures as discussed above. The reduction in chromophore content at λ_{max}~390 nm cannot entirely be explained by the elimination of these structures since sulfonation and hydrogen peroxide bleaching eliminate most of the structures of the coniferaldehyde and quinonoid type (cf. *69*). Hydroxystilbenes, introduced in the lignin moiety during high-yield pulping and alkaline bleaching conditions (*59,70,71*), have been proposed as the leucochromophores that, to a large extent, are responsible for the initial discoloration of bleached high-yield pulps (*60*, cf. *58*). Simple stilbenes have an absorption maximum at about 330 nm in solution, but it is possible that this maximum can be shifted to higher wavelengths when incorporated in the lignin macromolecule due to steric and electronic effects of substituent groups. Zhang and Gellerstedt (*14*) reported a red shift of the UV/VIS absorption maxima of quinone and

stilbene model compounds in the solid state (on filter paper or on bleached GWP or CTMP) compared with the absorption in solution. The red shift was 26 nm for a hydroxystilbene model and between 32 and 148 nm for compounds of the quinonoid type, an effect charge transfer complexes (quinone-phenol) might account for (*14,* cf. *72,73*).

Acetylated Pulps. It is known that acetylation influences brightness differently depending on the type of mechanical pulp derivatized (*30,48,* Paulsson, M.; Ragauskas, A.J. *Nord. Pulp Pap. Res. J.*, in press). Figure 6 shows the UV/VIS absorption spectra (acetylated - unacetylated) for the two tested pulps. During acetylation of aspen CTMP, a substantial increase in absorption is seen in the entire wavelength range 350-700 nm with maxima at approximately 370 and 430 nm. Acetylation of the spruce CTMP not only induced a discoloration, indicated by the absorption increase at λ>410 nm, but also a bleaching at wavelengths below 410 nm (maximum at approximately 385 nm). The decrease at 385 nm could possibly be explained by the removal of a hydroxystilbene structure (cf. the discussion above dealing with a red shift of the absorption maxima of stilbenes in the solid state). The peaks at 370 and 430 nm could result from the characteristic UV absorption of methoxylated *para*-quinones and visible absorption of *ortho*-quinones, respectively. The absorption peak at 455 nm is close to the absorption peak of a stilbene *ortho*-quinone structure incorporated on bleached CTMP (λ_{max}=460 nm) (*14*).

Irradiated Acetylated Pulps. Figures 4 and 5 show the effects of different irradiation times and irradiation sources on the UV/VIS absorption difference spectra of acetylated aspen CTMP and acetylated spruce CTMP.

It was interesting to see if acetylation, an efficient way to retard yellowing of different types of high-yield pulps, fundamentally changed the photochemistry or only slowed down the rate of chromophore formation, as judged from the UV/VIS absorption spectra. The acetylated aspen CTMP, irradiated with the UV-fluorescent lamps, generated an apparent absorption maximum in the same region as the unacetylated CTMP (λ, 370 nm, Figure 4a). No shoulder at 415 nm was, however, observed, and the increase in absorption was less in the whole UV-visible region. The UV/VIS-fluorescent light source induced a photobleaching in the visible range. The absorption in the UV-part of the spectra was also less and shifted about 20 nm toward shorter wavelengths (Figure 4b). The brightness values were 79-80% for the acetylated sheets compared to 60% for the control after an intense aging for 312 hours. The reduced absorption at λ_{max} just below 400 nm (extending into the visible range) indicates that some of the colored structures formed on acetylation of high-brightness aspen CTMP most likely are readily photobleachable when subjected to a light source emitting light in the visible range. Also, the acetylated spruce CTMP, irradiated with the UV/VIS-fluorescent lamps, removed structures contributing to the absorption just below 400 nm. The apparent absorption maximum at 425 nm observed for irradiated unacetylated spruce CTMP was essentially nonexistent after acetylation, except for the low derivatized CTMP (acetyl content, 4.4%, see Figure 5b).

These results indicate that acetylation slows down the UV-light induced reactions as seen for the UV-lamps aged CTMPs. However, acetylation promotes photobleaching reactions when subjected to an irradiation source emitting light in both the ultraviolet and visible regions, an effect that contributes to the improved stability toward light-induced aging. It is evident that measurements of brightness do not give a complete and accurate description of a complicated photochemical process such as the discoloration of lignin-containing materials. These results also indicate that different photochemical reactions occur, depending on the light source used for reversion, for acetylated pulps as well as for untreated pulps. It is therefore extremely important to use a light source that mimics the actual aging conditions as closely as possible if an accurate picture of the yellowing phenomenon is going to be obtained. Further studies,

using both unacetylated and acetylated model compounds incorporated on different types of high-yield pulps, are needed to fully explain the changes in the absorption difference spectra of acetylated and/or irradiated high-yield pulps.

Conclusions

Acetylation of aspen CTMP was found to generate a substantial increase in absorption in the entire wavelength region of 350-700 nm with maxima at approximately 370 and 430 nm, whereas the changes that took place during acetylation of the spruce CTMP were manifested as a decrease in absorption at wavelengths below 410 nm (maximum at 385 nm) and an increase in the absorption band centered at 455 nm.

UV-irradiation of aspen CTMP introduced chromophores with an absorption maximum near 370 nm and with a shoulder at approximately 415 nm. When aspen CTMP was irradiated with the UV/VIS lamps, a slight shift in the absorption peak to shorter wavelengths (λ_{max}~360 nm) together with less absorption in the visible range was observed. The absorption difference spectra of UV-irradiated spruce CTMP displayed two absorption bands at 330 and 425 nm. In addition to these two bands, UV/VIS-irradiation induced photobleaching in the UV-part of the spectra extending into the visible range (λ_{max}~390 nm). Acetylation of the pulps slowed down the UV-light induced chromophore formation, but could also promote photobleaching if the acetylated pulps were subjected to both UV-radiation and visible light.

It is difficult to assign the changes seen in the UV/VIS spectra to the formation/destruction of chromophoric and leucochromophoric structures in the lignin since (i) most absorption data are given for simple model compounds in solution, and it is likely that the position of the absorption peeks may be different in the solid phase, and (ii) the position of absorption maxima of the chromophoric and leucochromophoric structures may be shifted when incorporated in the lignin macromolecule. Further studies are therefore needed to determine the absorption characteristics of several classes of important structures when incorporated in different types of high-yield pulps.

Acknowledgments

Financial support for this work was provided by the Member Companies of the Institute of Paper Science and Technology, USDA Improved Utilization of Wood and Wood Fiber (Contract No. 96-35103-3800), and The Gunnar and Lillian Nicholson Graduate Fellowship and Faculty Exchange Fund.

Literature Cited

1. Heitner, C.; Schmidt, J.A. *Proc. 6th Int. Symp. Wood Pulp. Chem.*, Melbourne, Australia. April 29-May 3, **1991**; Vol. 1, 131.
2. Heitner, C. In *Photochemistry of Lignocellulosic Materials*; Heitner, C.; Scaiano, J.C., Eds.; ACS Symposium Series 531; ASC: Washington, D.C., USA, **1993**; Chapter 1, 2.
3. Leary, G.J. *J. Pulp Pap. Sci.* **1994**, *20*:6, J154.
4. Nolan, P.; Van den Akker, J.A.; Wink, W.A. *Paper Trade J.* **1945**, *121*:11, 33.
5. Andtbacka, A.; Holmbom, B.; Gratzl, J.S. *Proc. 5th Int. Symp. Wood Pulp. Chem.*, Raleigh, N.C., USA. May 22-25, **1989**; Vol. 1, 347.
6. Forsskåhl, I.; Janson, J. *Proc. 6th Int. Symp. Wood Pulp Chem.*, Melbourne, Australia. April 29-May 3, **1991**; Vol. 1, 255.

7. Andrady, A.L.; Song, Y.; Parthasarathy, V.R.; Fueki, K.; Torikai, A. *Tappi J.* **1991**, *74*:8, 162.
8. Forsskåhl, I.; Tylli, H. In *Photochemistry of Lignocellulosic Materials*; Heitner, C.; Scaiano, J.C., Eds.; ACS Symposium Series 531; ACS: Washington, D.C., USA, **1993**; Chapter 3, 45.
9. Andrady, A.L.; Searle, N.D. *Tappi J.* **1995**, *78*:5, 131.
10. Heitner, C.; Min, T. *Cellul. Chem. Technol.* **1987**, *21*:3, 289.
11. Lebo, S.E.; Lonsky, W.F.W.; McDonough, T.J.; Medvecz, P.J.; Dimmel, D.R. *J. Pulp Pap. Sci.* **1990**, *16*:5, J139.
12. Zhu, J.H.; Olmstead, J.A.; Gray, D.G. *J. Wood Chem. Technol.* **1995**, *15*:1, 43.
13. Schmidt, J.A.; Kimura, F.; Gray, D.G. *Res. Chem. Intermed.* **1995**, *21*:3-5, 287.
14. Zhang, L.; Gellerstedt, G. *Proc. 3rd European Workshop on Lignocellulosics and Pulp*, Stockholm, Sweden. August 28-31, **1994**; 293.
15. Zhang, L.; Gellerstedt, G. *Acta Chem. Scand.* **1994**, *48*:6, 490.
16. Hemmingson, J.A.; Morgan, K.R. *Holzforschung* **1990**, *44*:2, 127.
17. Capretti, G.; Castellan, A.; Choudhury, H.; Davidson, R.S.; Noutary, C.; Origgi, S.; Trichet, V. *Proc. 3rd European Workshop on Lignocellulosics and Pulp*, Stockholm, Sweden. August 28-31, **1994**; 159.
18. Schmidt, J.A.; Heitner, C. J. *Wood Chem. Technol.* **1995**, *15*:2, 223.
19. Pan, X.; Ragauskas, A.J. *Proc. 9th Int. Symp. Wood Pulp. Chem.*, Montréal, Canada. June 9-12, **1997**; 97-1.
20. Argyropoulos, D.S.; Heitner, C.; Schmidt, J.A. *Res. Chem. Intermed.* **1995**, *9*:3-5, 263.
21. Sjöholm, R.; Holmbom, B.; Åkerback, N. *J. Wood Chem. Technol.* **1992**, *12*:1, 35.
22. Forsskåhl, I.; Maunier, C. In *Photochemistry of Lignocellulosic Materials*; Heitner, C.; Scaiano, J.C., Eds.; ACS Symposium Series 531; ACS: Washington, D.C., USA, **1993**; Chapter 12, 156.
23. Robert, S.; Daneault, C. *J. Wood Chem. Technol.* **1995**, *15*:1, 113.
24. Gierer, J.; Lin, S.Y. *Svensk Papperstidn.* **1972**, *75*:7, 233.
25. Neumann, M.G.; Machado, A.E.H. *J. Photochem. Photobiol., B.* **1989**, *3*:4, 473.
26. Ek, M. *Some Aspects on the Mechanisms of Photoyellowing of High-yield Pulps*; Royal Institute of Technology, Stockholm, Sweden, **1992**; Ph.D. Thesis.
27. Castellan, A.; Nourmamode, A.; Jaeger, C.; Forsskåhl, I. *Nord. Pulp Pap. Res. J.* **1993**, *8*:2, 239.
28. Forsskåhl, I.; Tylli, H.; Olkkonen, C. *Proc. 7th Int. Symp. Wood Pulp. Chem.*, Beijing, P.R. China. May 25-28, **1993**, Vol. *2*, 750.
29. Paulsson, M.; Simonson, R.; Westermark, U. *Nord. Pulp Pap. Res. J.* **1994**, *9*:4, 232.
30. Paulsson, M.; Simonson, R.; Westermark, U. *Nord. Pulp Pap. Res. J.* **1996**, *11*:4, 227.
31. Giertz, H.W. *Svensk Papperstidn.* **1945**, *48*:13, 317.
32. Janson, J.; Forsskåhl, I. *Nord. Pulp Pap. Res. J.* **1989**, *4*:3, 197.
33. Johnson, R.W. *Tappi J.* **1989**, *72*:12, 181.
34. Waymouth, J.F. In *Encyclopedia of Physical Science and Technology*; Meyers, R.A., Ed.; Academic Press Inc.: San Diego, CA, USA, **1992**; Vol. 8; 697.
35. Merrigan, J.A. *Sunlight to Electricity*; The MIT Press: MA, USA, **1975**; Chapter 3, 41.
36. Lewis, H.F.; Reineck, E.A.; Fronmuller, D. *Paper Trade J.* **1945**, *121*:8, 44.
37. Francis, R.C.; Dence, C.W.; Alexander, T.C.; Agnemo, R.; Omori, S. *Tappi J.* **1991**, *74*:12, 127.
38. Forsskåhl, I.; Janson, J. *Pap. Puu* **1992**, *74*:7, 553.
39. Paulsson, M.; Simonson, R.; Westermark, U. *Nord. Pulp Pap. Res. J.* **1995**, *10*:1, 62.

40. Wang, J.; Heitner, C.; Manley, R.St.J. *Proc. 7th Int. Symp. Wood Pulp. Chem.*, Beijing, P.R. China. May 25-28, **1993**; Vol. 2, 740.
41. Wang, J.; Heitner, C.; Manley, R.St.J. *Proc. 8th Int. Symp. Wood Pulp. Chem.*, Helsinki, Finland. June 6-9, **1995**; Vol. 3, 27.
42. Bruce, J.M. *Quart. Rev.* **1967**, *21*:2, 405.
43. Bruce, J.M. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; John Wiley & Sons Ltd.: Bristol, G.B., **1974**; Vol. 1, Chapter 9, 465.
44. Ragauskas, A.J. In *Photochemistry of Lignocellulosic Materials*; Heitner, C.; Scaiano, J.C., Eds.; ACS Symposium Series 531; ACS: Washington, D.C., USA, **1993**; Chapter 5, 77.
45. Schmidt, J.A.; Kimura, F.; Gray, D.G. *Proc. 8th Int. Symp. Wood Pulp. Chem.*, Helsinki, Finland. June 6-9, **1995**; Vol. 1, 443.
46. Callow, H.J. *Nature* **1947**, *159*:4035, 309.
47. Callow, H.J.; Speakman, J.B. *J. Soc. Dyers Col.* **1949**, *65*:12, 758.
48. Manchester, D.F.; McKinney, J.W.; Pataky, A.A. *Svensk Papperstidn.* **1960**, *63*:20, 699.
49. Andrews, D.H.; Des Rosiers, P. *Pulp Pap. Mag. Can.* **1966**, *67*:C, T119.
50. Lorås, V. *Pulp Pap. Mag. Can.* **1968**, *69*:2, 57.
51. Ek, M.; Lennholm, H.; Lindblad, G.; Iversen, T. *Nord. Pulp Pap. Res. J.* **1992**, *7*:3, 108.
52. Hirashima, H.; Sumimoto, M. *Mokuzai Gakkaishi* **1987**, *33*:1, 31.
53. Pan, X.; Lachenal, D.; Lapierre, C.; Monties, B. *J. Wood Chem. Technol.* **1992**, *12*:2, 135.
54. Pan, X.; Lachenal, D.; Lapierre, C.; Monties, B.; Neirinck, V.; Robert, D. *Holzforschung* **1994**, *48*:5, 429.
55. Agarwal, U.P.; McSweeny, J.D. *Proc. 8th Int. Symp. Wood Pulp. Chem.*, Helsinki, Finland. June 6-9, **1995**; Vol. 1, 435.
56. Agarwal, U.P.; Atalla, R.H.; Forsskåhl, I. *Holsforschung* **1995**, *49*:4, 300.
57. Paulsson, M.; Li, S.; Lundquist, K.; Simonson, R.; Westermark, U. *Nord. Pulp Pap. Res. J.* **1996**, *11*:4, 220.
58. Castellan, A.; Colombo, N.; Nourmamode, A.; Zhu, J.H.; Lachenal, D.; Davidson, R.S.; Dunn, L. *J. Wood Chem. Technol.* **1990**, *10*:4, 461.
59. Gellerstedt, G.; Zhang, L. *J. Wood Chem. Technol.* **1992**, *12*:4, 387.
60. Gellerstedt, G.; Zhang, L. In *Photochemistry of Lignocellulosic Materials*; Heitner, C.; Scaiano, J.C., Eds.; ACS Symposium Series 531; ACS: Washington, D.C., USA, **1993**; Chapter 10, 129.
61. Schmidt, J.A.; Heitner, C. *Tappi J.* **1993**, *76*:2, 117.
62. Hirashima, H.; Sumimoto, M. *Mokuzai Gakkaishi* **1986**, *32*:9, 705.
63. Fornier de Violet, P.; Nourmamode, A.; Colombo, N.; Castellan, A. *Cellul Chem. Technol.* **1989**, *23*:5, 535.
64. Forsskåhl, I.; Janson, J. *Nord. Pulp Pap. Res. J.* **1991**, *6*:3, 118.
65. Schmidt, J.A.; Heitner, C. *J. Wood Chem. Technol.* **1991**, *11*:4, 397.
66. Schmidt, J.A.; Heitner, C. *J. Wood Chem. Technol.* **1993**, *13*:3, 309.
67. Schmidt, J.A.; Heitner, C. *Proc. 9th Int. Symp. Wood Pulp. Chem.*, Montréal, Canada. June 9-12, **1997**; 98-1.
68. Adler, E.; Lundquist, K. *Acta Chem. Scand.* **1961**, *15*:1, 223.
69. Dence, C.W. In *Pulp Bleaching - Principles and Practice*; Dence, C.W.; Reeve, D.W., Eds.; TAPPI Press: Atlanta, GA, USA, **1996**; Section III, Chapter 4, 161.
70. Gellerstedt, G.; Agnemo, R. *Acta Chem. Scand.* **1980**, *B34*:6, 461.
71. Wu, Z.H.; Matsuoka, M.; Lee, D.Y.; Sumimoto, M. *Mokuzai Gakkaishi* **1991**, *37*:2, 164.
72. Furman, G.S.; Lonsky, W.F.W. *IPC Technical Paper Series 198*, **1986**.
73. Furman, G.S.; Lonsky, W.F.W. *J. Wood Chem. Technol.* **1988**, *8*:2, 165.

Figure Captions

Figure 1. The change in TAPPI brightness of untreated and acetylated spruce CTMP (O) and aspen CTMP (□) after aging with the UV-fluorescent lamps. The spectral energy distribution of the UV-fluorescent lamps is given in **a**. Legends (acetyl content): (····O····), 4.6%; (---O---), 9.4%; (····□····), 4.1%; (---□---), 9.7%.

Figure 2. The change in TAPPI brightness of untreated and acetylated spruce CTMP (O) and aspen CTMP (□) after aging with the UV/VIS-fluorescent lamps. The spectral energy distribution of the UV/VIS-fluorescent lamps (solid line) and standard "cool white" fluorescent color (broken line) is given in **a**. Legends (acetyl content): (····O····), 4.6%; (---O---), 9.4%; (····□····), 4.1%; (---□---), 9.7%.

Figure 3. The change in brightness of untreated and acetylated spruce CTMP (O) and aspen CTMP (□) after aging with the xenon lamp. The spectral energy distribution of the xenon lamp (solid line) and natural daylight (dotted line) is given in **a**. Legends (acetyl content): (····O····), 4.6%; (---O---), 9.4%; (····□····), 4.1%; (---□---), 9.7%.

Figure 4. Absorption difference spectra ($\Delta ABS = ABS_{irradiated} - ABS_{unirradiated}$) of acetylated and untreated hydrogen-peroxide-bleached aspen CTMP after aging with UV-lamps (**a**) and UV/VIS-lamps (**b**). Legends: (—), control; (····), acetylated - 3.9%; (- -), acetylated - 8.1%.

Figure 5. Absorption difference spectra ($\Delta ABS = ABS_{irradiated} - ABS_{unirradiated}$) of acetylated and untreated hydrogen-peroxide-bleached spruce CTMP after aging with UV-lamps (**a**) and UV/VIS-lamps (**b**). Legends: (—), control; (····), acetylated - 4.4%; (- -), acetylated - 9.6%.

Figure 6. Absorption difference spectra ($\Delta ABS = ABS_{acetylated} - ABS_{unacetylated}$) of aspen and spruce CTMPs after acetylation. The numbers in brackets denote the acetyl content (% by mass).

Table I. Change in optical properties on acetylation and light-induced aging of hydrogen-peroxide-bleached pulps. Acetyl content (% by mass) are given within parentheses.

Pulp		TAPPI brightness (%)	PC_1[a]	UV-lamps Irradiation time: 4 h			UV/VIS-lamps Irradiation time: 216 h			Xenon lamp Irradiation time: 40 h		
				TAPPI brightness	PC_2[b]	Δk[c]	TAPPI brightness	PC_2[b]	Δk[c]	Brightness[d]	PC_2[b]	Δk[c]
CTMP, spruce												
Control	(0.5)	78.2	0.0	49.6	22.5	10.9	48.2	24.8	12.0	48.4	24.4	11.8
Acetylated	(4.6[e])	76.3	0.6	53.0	17.2		63.9	6.5		55.5	14.4	
	(9.4[e])	75.6	0.9	59.0	10.3		73.5	0.8		61.5	8.4	
CTMP, aspen												
Control	(0.6)	84.3	0.0	55.6	16.2	6.2	66.5	7.0	2.7	58.2	13.4	5.1
Acetylated	(4.1[e])	81.0	0.9	59.0	12.0		77.0	1.3		64.0	8.2	
	(9.7[f])	74.6	3.1	63.8	6.1		81.5	-2.1		70.7	2.3	

[a]The post-color (PC_1) number at 457 nm (due to acetylation) was calculated according to (*31*).
[b]The post-color (PC_2) number at 457 nm (due to irradiation) was calculated according to (*31*).
[c]The change in light absorption (Δk) was calculated from the PC_2-value with the assumption of constant light scattering (*33*).
[d]Brightness measured with an Elrepho 2000 spectrophotometer. This instrument uses a diffuse light source and measures the reflected light at a 0°viewing angle, i.e., the "Elrepho" brightness cannot directly be translated to TAPPI brightness that is determined with an instrument employing a directional light source (incident angle of 45°) and measures the reflected light at a 0°viewing angle. The difference in measured brightness was, however, small (less than 1 brightness unit).
[e]Acetylation temperature, 100°C.
[f]Acetylation temperature, 110°C.

Figure 1

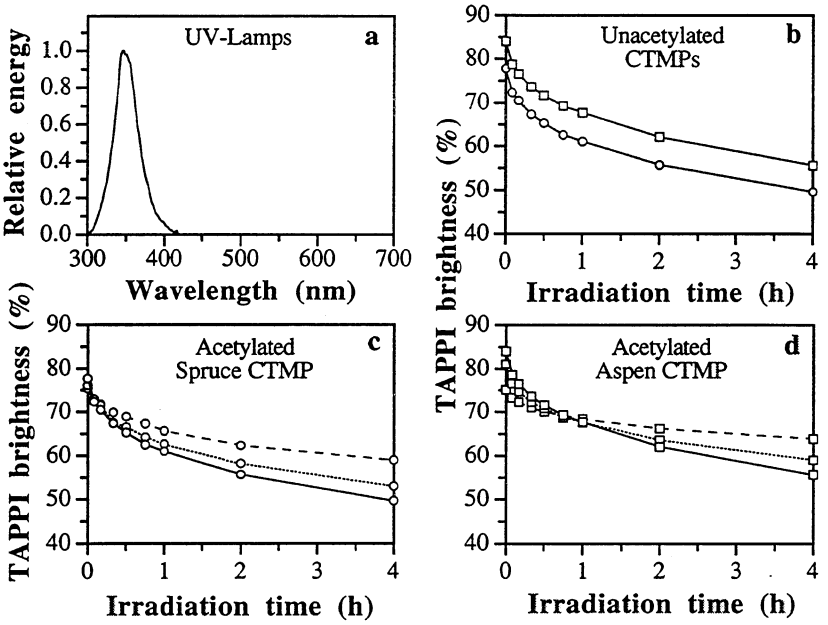

UV-Lamps
a
Relative energy
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
Wavelength (nm)
Unacetylated
CTMPs
b
TAPPI brightness (%)
90
80
70
60
50
40
0
1
2
3
4
Irradiation time (h)
Acetylated
Spruce CTMP
c
TAPPI brightness (%)
Irradiation time (h)
Acetylated
Aspen CTMP
d
TAPPI brightness (%)
Irradiation time (h)

Figure 2

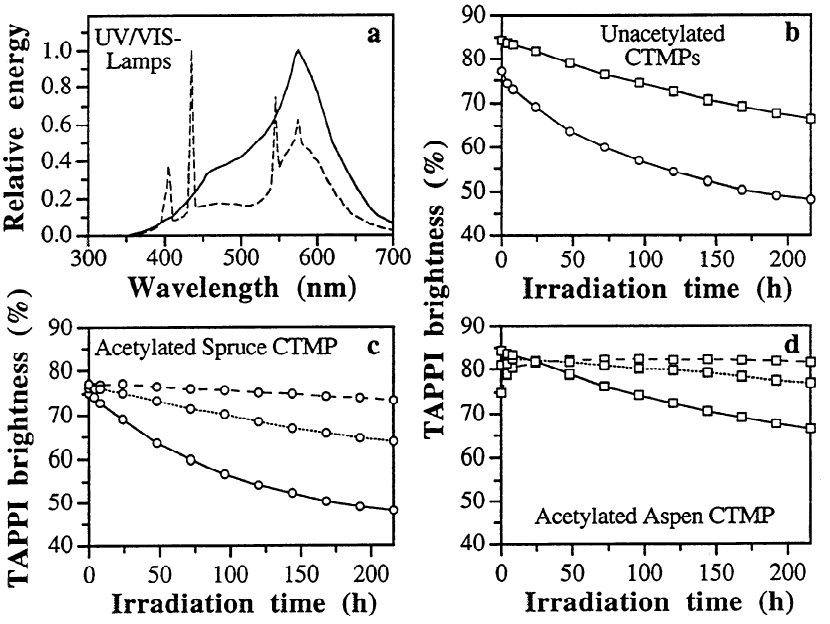

a
UV/VIS-
Lamps
Relative energy
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
Wavelength (nm)
b
Unacetylated
CTMPs
TAPPI brightness (%)
90
80
70
60
50
40
0
50
100
150
200
Irradiation time (h)
c
Acetylated Spruce CTMP
TAPPI brightness (%)
Irradiation time (h)
d
Acetylated Aspen CTMP
TAPPI brightness (%)
Irradiation time (h)

Figure 3

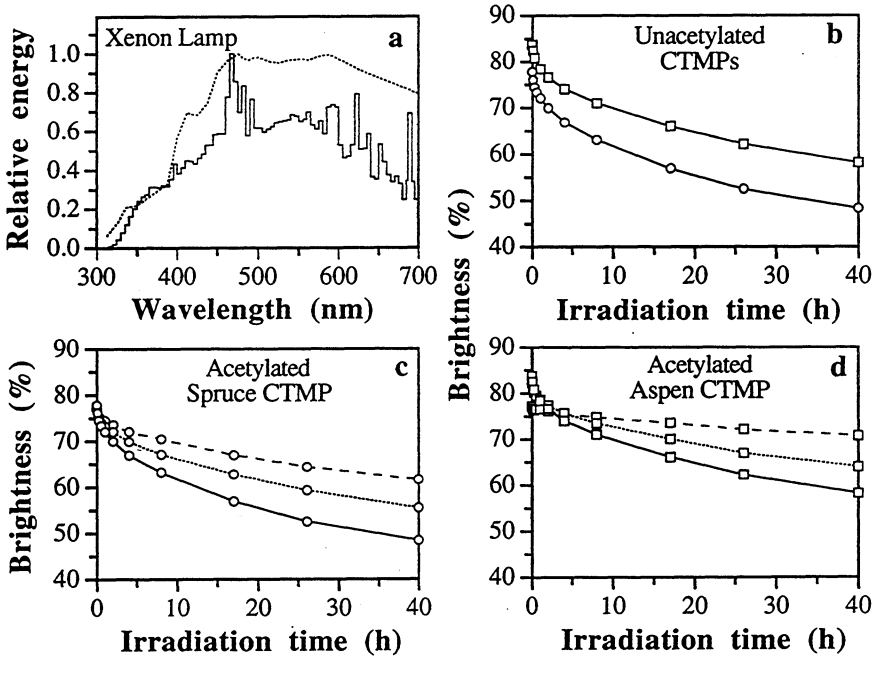

Xenon Lamp
a
Relative energy
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
Wavelength (nm)
Unacetylated
CTMPs
b
Brightness (%)
90
80
70
60
50
40
0
10
20
30
40
Irradiation time (h)
Acetylated
Spruce CTMP
c
Brightness (%)
Irradiation time (h)
Acetylated
Aspen CTMP
d
Brightness (%)
Irradiation time (h)

Figure 4

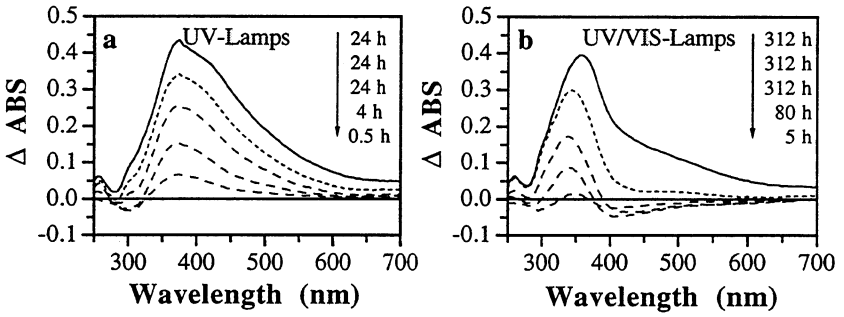

a
UV-Lamps
24 h
24 h
24 h
4 h
0.5 h
Δ ABS
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
300
400
500
600
700
Wavelength (nm)
b
UV/VIS-Lamps
312 h
312 h
312 h
80 h
5 h
Δ ABS
Wavelength (nm)

Figure 5

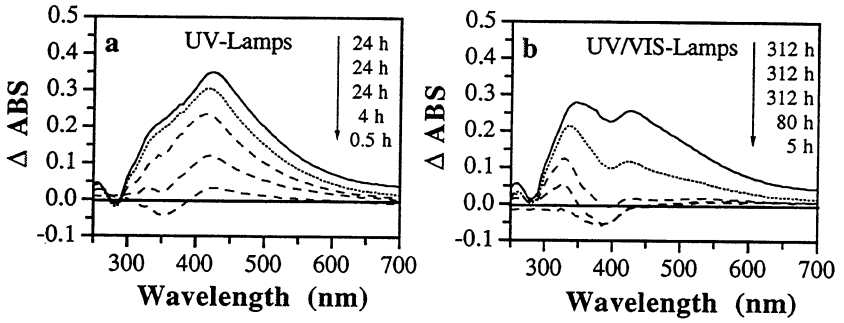
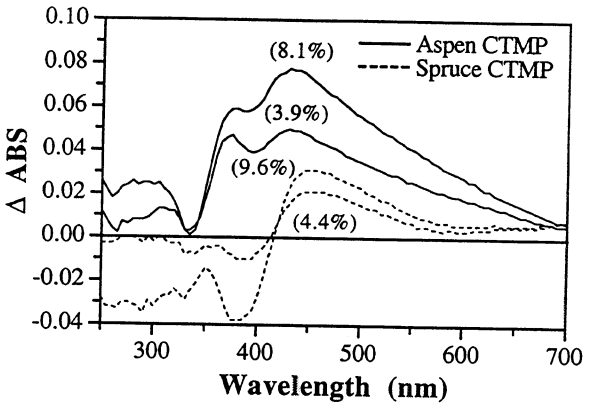

a
UV-Lamps
24 h
24 h
24 h
4 h
0.5 h
Δ ABS
Wavelength (nm)
b
UV/VIS-Lamps
312 h
312 h
312 h
80 h
5 h
Δ ABS
Wavelength (nm)

Figure 6


0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
Δ ABS
300
400
500
600
700
Wavelength (nm)
(8.1%)
(3.9%)
(9.6%)
(4.4%)
Aspen CTMP
Spruce CTMP